

## Novel (Glycerol)borate-Based Ionic Liquids: An Experimental and Theoretical Study

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A series of newly designed (glycerol)borate based ionic liquids were synthesized and characterized. The synthesis of these ionic liquids involves, first, the preparation of the bis(glycerol)boric acid(s) followed by neutralization with the appropriate base, [cat]<sup>+</sup>[OH]<sup>-</sup>. Ionic liquids bearing inorganic (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) or organic cations have been prepared and characterized. The ability of the bis(glycerol)borate anions to undergo dissociation reaction in the presence of water, depending on cation nature, was investigated by NMR. Theoretical calculations were also performed to evaluate the relative stability of the possible bis(glycerol)borate isomers as nude ions or as ion pairs with Li<sup>+</sup>, Na<sup>+</sup>, and H<sup>+</sup>. Important information about the structural features of H[Gly<sub>2</sub>B] useful to rationalize the chemical behavior have been obtained.

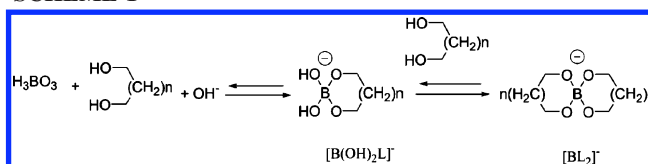
## Introduction

Glycerol (1,2,3-propanetriol), an organic molecule isolated by heating fats in the presence of ash to produce soap, is an industrial chemical with tens of applications. Its synthetic production from epichlorohydrin obtained from propylene started in the late 1940s and for many years glycerol has been a petrochemical industry product. Today, however, glycerol is obtained in large surplus as by product (10% in weight) in manufacturing biodiesel fuel by transesterification of seed oils with methanol. Consequently, not only the necessity to produce glycerol from propylene is finished but it has become a priority to find new applications of glycerol and its derivatives.<sup>1</sup>

With a focus on recent developments in the conversion of glycerol into value-added chemicals, we tried to transform glycerol in sustainable ionic species, cations<sup>2</sup> or anions. Borate esters of polyhydroxy compounds and their potential for separation or application as additives are being explored for a long time.<sup>3</sup> In particular, borate esters of glycerol are highly present in the patent literature; they are used as additives in ink-jet recording media, antistatic multilayer polyester films, heat-developable photographic materials, and so on.<sup>4</sup> Whereas alcohols (ROH) react with boric acid (B(OH)<sub>3</sub>) to yield neutral esters like B(OR)<sub>3</sub>, polyols form chelates, whose structure depends on the relative positions of the available hydroxyl groups of the ligand. Both five- and six-membered monodiol [B(OH)<sub>2</sub>L]<sup>-</sup> and bis-diol [BL<sub>2</sub>]<sup>-</sup> complexes, in an equilibrium with the borate anion, have been proposed (Scheme 1).<sup>5</sup> In water, the equilibrium constants characterizing the two steps formation of bis-diol [BL<sub>2</sub>]<sup>-</sup> complexes depend on diol structure, pH, and temperature.<sup>6</sup>

In this paper, we report on our attempts to synthesize ionic liquids (ILs) having bis(glycerol)borate(s) as anion. The term IL defines a large class of compounds constituted exclusively by ions, which are liquid at or near room temperature (for definition, below 100 °C). The ionic nature confers to these compounds unique properties that make them suitable for large

## SCHEME 1



scale applications; solvents, catalysts, materials for separations and gas capture, advanced heat transfer fluids, lubricants, antistatics, and so on.<sup>7</sup> Moreover, due to the low vapor pressure, nonflammability, and high thermal stability, ILs are considered “greener” than many other generally employed solvents or catalytic systems. However, recently some doubts about the green character of ILs has emerged; many ILs arise from fossil oil, and some of these have a significant environmental impact, in particular on the aquatic ecosystem.<sup>8</sup> The use of low cost no-toxic renewable compounds might therefore represent a winning strategy to obtain sustainable ILs<sup>9</sup> favoring at the same time the large scale application of byproducts (such as glycerol) which are becoming waste.

Here, we give details on the possibility to synthesize ILs based on bis(glycerol)borates evidencing how the stability of this anion is affected by the cation nature and by the environmental conditions and what are the limits and potentialities of application of these salts.

## Results and Discussion

**Synthesis and Characterization of (Glycerol)borates.** The bis(glycerol)boric acid, H[Gly<sub>2</sub>B], was synthesized using the synthetic route described in a recent patent.<sup>10</sup> Glycerol was added to the appropriate quantity of boric acid in toluene, and the reaction was allowed to proceed at reflux temperature (Scheme 2).

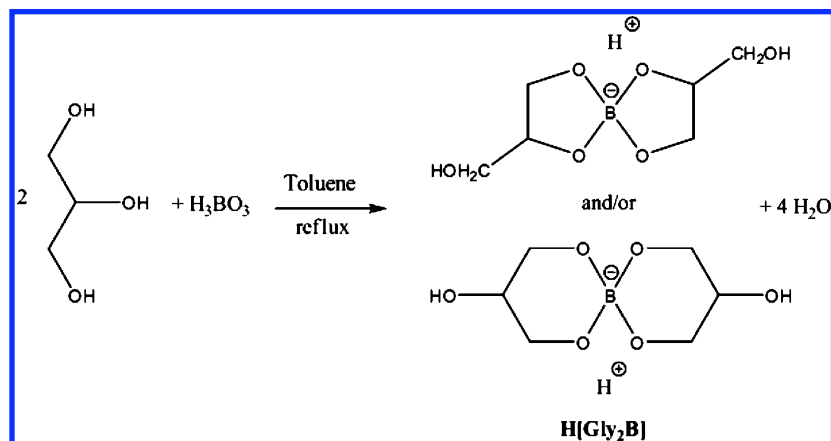
The byproduct water was continuously removed from the reaction by azeotropic distillation, obtaining a high viscous uncolored liquid. Electrospray ionization mass spectrometry (ESI-MS) spectrum of a sample dissolved in acetonitrile was characterized by the presence in the negative mode of a strong peak at *m/e* 191 attributable to a bis(glycerol)borate, whereas

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## SCHEME 2



<sup>11</sup>B NMR spectroscopy on the same sample evidenced the presence of two partially superimposed peaks in ca. 1:4 ratio at 28.01 and 23.8 ppm, respectively. Although these values are significantly different from that characterizing of H<sub>3</sub>BO<sub>3</sub> in acetonitrile (25.0 ppm), however, both peaks present typical chemical shift values of a trigonal boron. Moreover, due to the high bandwidth it was not possible to exclude the presence of minor amounts of free boric acid as well as the occurrence of dynamic processes. On the other hand, <sup>13</sup>C NMR spectrum was characterized by the presence of two signals attributable to free glycerol (64.13 and 73.12) besides three other large signals at 65.3, 67.7, and 67.9, probably due to “bounded” glycerol. The small amount of water, generally present in CD<sub>3</sub>CN, was probably sufficient to start up the hydrolysis process. Related to this feature, it is noteworthy that the NMR spectra of the same sample in D<sub>2</sub>O, registered some minutes after dissolution, were characterized practically by the exclusive presence of signals attributable to H<sub>3</sub>BO<sub>3</sub> and glycerol suggesting a very low stability (if any) of bis(glycerol)boric acid in this medium.

Different was the situation in the presence of a base. The addition of an equivalent of KOH, NaOH, or LiOH to the water solution of bis(glycerol)boric acid (or to the 1:2 mixture of H<sub>3</sub>BO<sub>3</sub> and glycerol) gave the corresponding sodium, potassium, and lithium bis(glycerol)borates. <sup>11</sup>B NMR spectrum in D<sub>2</sub>O of the sample obtained by addition of NaOH was characterized by the presence of two intense peaks at 10.67 and 6.67 ppm, respectively (Figure 1).

On the basis of the chemical shift values reported<sup>5</sup> for several five- and six-membered mono and bis-chelate complexes of

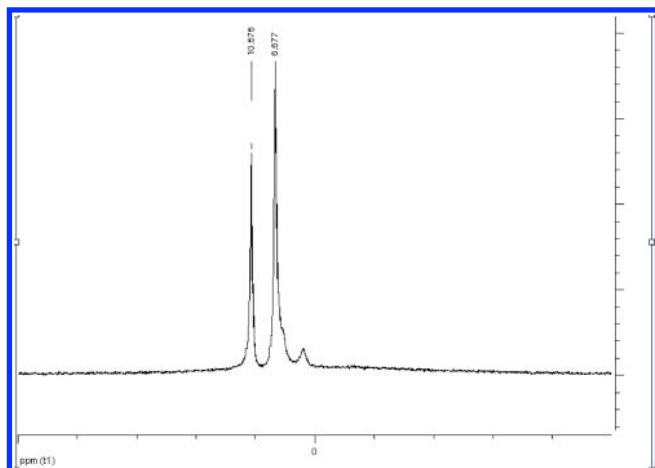
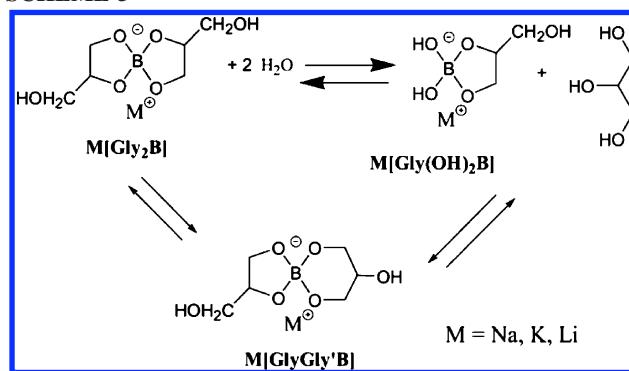


Figure 1. <sup>11</sup>B NMR spectrum of sodium salt(s).

## SCHEME 3



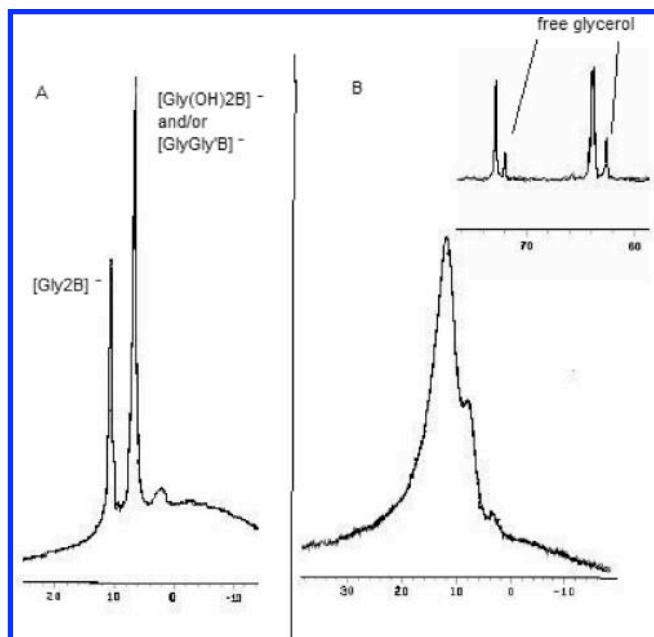
polyols with boric acid ([B(OH)<sub>2</sub>L]<sup>-</sup> and [BL<sub>2</sub>]<sup>-</sup>) the peak at 10.67 ppm could be assigned to the five-membered bis(glycerol)borate, for this isomer the values range from 14.0 to 9.8 ppm. At variance the attribution of the peak at 6.67 ppm appeared more controversial on the basis of the sole <sup>11</sup>B NMR spectrum; both the five-membered mono(glycerol)borate and the mixed five-six-membered bis(glycerol)borate (Scheme 3) could give a peak around this chemical shift value.<sup>5</sup> However, the presence in the <sup>13</sup>C NMR spectrum of the same sample of two signals at 71.6 and 62.05 ppm, attributable to free glycerol, besides two other groups of signals centered at 63.5 and 72.5 ppm, suggested the presence in solution of the mono(glycerol)borate, although these latter data were not able to exclude also the presence of the mixed five-six-membered bis(glycerol)borate.

It is noteworthy that the intensity of the signals at 63.5 and 72.5 increased with respect to those of free glycerol increasing the sample concentration. Concentration affected also the <sup>11</sup>B NMR spectrum modifying the relative intensity of the two peaks and their bandwidth; peaks tended to merge at an intermediate chemical shift value. In agreement with the above-reported equilibria, water concentration determines the ratio between bis(glycerol)borate(s) and the mono(glycerol)borate, whereas ion pairing phenomena probably affect the interconversion between bis(glycerol)borate(s). Finally, it is to note that the <sup>11</sup>B NMR spectra of these salts seem to exclude the formation of significant amounts of the six-membered bis(glycerol)borate and of the corresponding mono(glycerol)borate; only a small peak attributable to these latter complexes around 2 ppm was evidenced.

The thermal properties of lithium, potassium and sodium salts were investigated using differential scanning calorimetry (DSC). The glass transition temperatures (*T*<sub>g</sub>) of K[Gly<sub>2</sub>B], Na[Gly<sub>2</sub>B], and Li[Gly<sub>2</sub>B] rise on decreasing the cation size (Table 1). It is

**TABLE 1: Thermal Properties of [Cat][Gly<sub>2</sub>B] Salts**

[Cat][Gly <sub>2</sub> B]	<i>T<sub>g</sub></i> (°C) <sup>a</sup>	Δ <i>C<sub>p</sub></i> (J/g °C)
Li[Gly <sub>2</sub> B]	78	0.639
Na[Gly <sub>2</sub> B]	75	1.26
K[Gly <sub>2</sub> B]	36	0.575

<sup>a</sup> Glass transition temperature.**Figure 2.** NMR spectra of tetrabutylammonium salt(s). (A) <sup>11</sup>B NMR spectrum of a diluted solution in D<sub>2</sub>O. (B) <sup>11</sup>B NMR and <sup>13</sup>C NMR (window) spectra of a concentrated solution in D<sub>2</sub>O.

however noteworthy that all salts are liquid below 100 °C and therefore can be considered as ILs. Consequently, the alkaline salts of bis(glycerol)borates represent one of the few reported<sup>11</sup> examples of ionic liquids characterized by an inorganic cation.

Although these salts based on metal cations may extend the possibilities of application of ILs, several attempts have also been carried out to synthesize bis(glycerol)borate based salts bearing organic cations. At the moment, the best procedure appears the treatment of a concentrated water solution of bis(glycerol)boric acid with an equimolar amount of [Cat]OH. Under these conditions, [Bu<sub>4</sub>N]OH gives a viscous liquid which has been identified on the basis of the NMR and ESI-MS spectra as [Bu<sub>4</sub>N][Gly<sub>2</sub>B]. However, in agreement with the behavior observed for the salts bearing a metal cation, the bis(glycerol)borate anion(s) undergoes to partial dissociation in the presence of relevant amounts of water. The <sup>11</sup>B and <sup>13</sup>C NMR spectra in D<sub>2</sub>O are consistent with the presence of mono(glycerol)borate and free glycerol besides bis(glycerol)borate(s) (Figure 2).

Also in this case the entity of anion hydrolysis depended on salt concentration; by increasing dilution we observed an increase in the signals of mono(glycerol)borate and free glycerol with respect the signals of bis(glycerol)borate(s). On the other hand, in the <sup>13</sup>C NMR spectrum of this salt dissolved in DMSO-*d*<sub>6</sub> the signals of glycerol were practically undetectable whereas the signals at 73.1, 65.5, and 63.1 were extremely large. A dynamic process, such as the relatively slow interconversion of the two bis(glycerol)borates (Scheme 2) might account of these latter spectral data.

It is noteworthy that all attempts to obtain imidazolium-based ILs through the generally used exchange reactions yielded salts

of moderate purity. The addition of 1-hydroxyethyl-3-methylimidazolium chloride ([HOetmim]Cl) to concentrated water solution of Na[Gly<sub>2</sub>B] gave, after water evaporation and elimination of NaCl by centrifugation, a viscous liquid identified on the basis of NMR spectra as [HOetmim][Gly<sub>2</sub>B]. The ESI-MS spectrum in negative mode confirmed the presence of the bis(glycerol)borate anion; however, a more accurate analysis of the clusters present in the positive mode evidenced the presence of residual chloride.

Analogously, [bmim][Gly<sub>2</sub>B] containing residual LiBr (or LiCl) was obtained by reaction of glycerol, H<sub>3</sub>BO<sub>3</sub>, LiCO<sub>3</sub>, and [bmim]Br (or [bmim][Cl]). Unfortunately, the tendency of [Gly<sub>2</sub>B]<sup>-</sup> to undergo hydrolysis in water solution, and the insolubility of these salts in many organic solvents, prevented the possibility to use exchange reactions to obtain highly pure ionic liquids (Scheme 4).

**Theoretical Calculations.** Scheme 3 gives a simplified representation of the structural features of mono and bis(glycerol)borates; for each complex are indeed possible several stereoisomers and/or conformers. Ab initio calculations have been therefore performed to evaluate the absolute stabilities of the possible bis(glycerol)borate complexes depending on counteranion (H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>). As previously mentioned, [Gly<sub>2</sub>B]<sup>-</sup> anion is characterized by four B–O bonds that are part of two cyclic systems. Glycerol can give five-membered (1,2 esterification) or six-membered (1,3 esterification) rings. While the relative rigidity of the five-membered ring determines the presence in solution of only one conformer, the six-membered ring can exist in the two well-known conformations, boat and chair. Chair is known to be the more stable conformer in simple hydrocarbons, for example cyclohexane and glucose. However, there are cases in which intramolecular interactions and/or formation of intermolecular complexes can lead to an inversion of the energetic order.<sup>12</sup> An inspection of the possible structures for the [Gly<sub>2</sub>B]<sup>-</sup> anion using a molecular CAD package<sup>13</sup> shows the following possibilities:

Structure 1: Two fused five-membered rings in a unique conformation, but with different orientations of the hydroxymethyl substituents. More in particular, since two conventional chiral centers are present on the glycerol moieties and the boron atom may be considered a further “spirane”-like chiral center, taking into account the symmetry of the system, three diastereomeric racemates should be present in solution (Scheme 5).

Structure 2. Two fused six-membered rings, both in the chair conformation.

Structure 3. Two fused six-membered rings in boat conformation, stabilized by intramolecular hydrogen bonds.

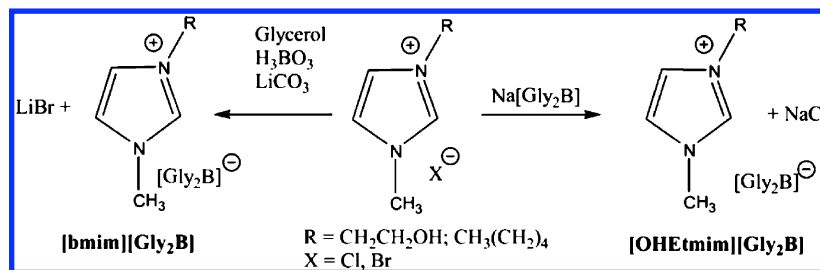
Structure 4. A hybrid structure with a five- and a six-membered ring. The last one in the boat conformation that allows the intramolecular hydrogen bonding.

Structure 5. Two six-membered rings: one in chair and the other one in boat conformation.

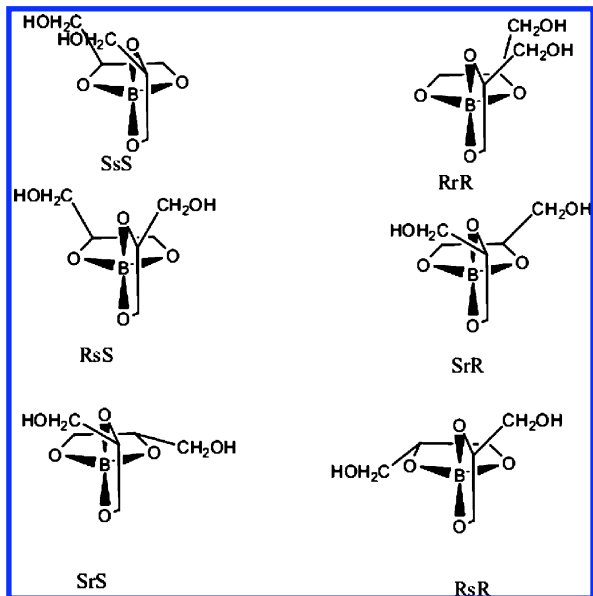
Structure 6. A hybrid structure with a five membered ring and a six membered ring. The last one in chair conformation. No intramolecular hydrogen bonding is allowed.

By consideration of the relevant number of possible structures, we reduced the list of isomers to investigate on the basis of some considerations. The spiro boron atom shows a tetrahedral coordination without remarkable distortions. The two rings bear always a single substituent: an OH group in  $\gamma$  position in the six-membered ring and a CH<sub>2</sub>OH group in  $\beta$  position in the five-membered systems. The  $\alpha$  position is always an esteric oxygen atom. In the six-membered ring having the chair conformation the OH substituent is very far from the other five

## SCHEME 4



## SCHEME 5



or six membered ring; no stabilization arising from intramolecular hydrogen bonding or destabilization due to steric interactions is possible. Thus, in this conformation the six-membered ring is unable to interact in an energetically relevant way with the other ring. We can reasonably argue that structures 5 and 6 do not show any specific chemical issue. The energies of these structures can be roughly estimated by averaging the energies of structures 2,3 and 1,2, respectively. On these bases, we skipped structures 5 and 6. Similar considerations can be done for the three diastereomeric racemates reported in Scheme 5. The two  $\text{CH}_2\text{OH}$   $\beta$  substituents are on two orthogonal rings, and therefore they cannot form ring to ring hydrogen bonding or cause destabilizing steric interactions in none of the possible six isomers. Thus, we decided to consider only one isomer (RrR, reported in Scheme 5) as representative of all stereoisomers; the energy differences among the three distereoisomer couples reported in Scheme 5 should be negligible, at least in comparison with the energy values characterizing the other structures.

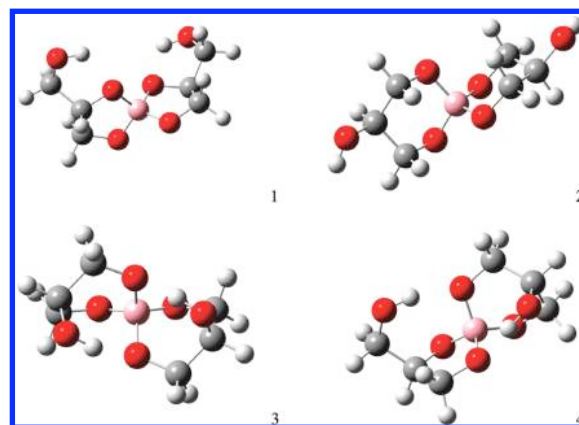
All the structures were fully optimized at the B3LYP/CEP-121G(d,p) level using the Gaussian 03 package.<sup>14</sup> This level of theory has been well tested to be reliable by some of the authors in other scientific papers.<sup>15</sup> A benchmark<sup>16</sup> of the CEP-121G(d,p) basis set against an all-electron basis shows that this basis set gives results comparable to the all-electrons basis sets like 6-311+(d,p) at a reduced computational cost (about 1.4–2.0). Furthermore, calculations on boron-containing molecules with same basis set and DFT functional showed good agreement with experimental results.<sup>17</sup>

Although structures 1, 2, and 3 of Figure 3 present a  $C_2$  symmetry we chose to not track symmetry during calculations to maintain all degrees of freedom. All structures remained very close to symmetric geometries during optimization procedures.

The relevant geometrical and energetic quantities relatives to structures 1–4 and to their complexes with  $\text{H}^+$ ,  $\text{Li}^+$ , and  $\text{Na}^+$  cations are reported in Table 2. All quantities included zero point energies. Structures of ions are reported in Figure 3.

First, we considered the energies of the isolated anions. The most stable structure was 4. This isomer is characterized by two hydrogen bonds. The donors are the hydrogen atoms of the free OH groups whereas the acceptors are the ester oxygen atoms; donor and acceptor belong to different rings. The same pattern is present in structure 3 (boat–boat). However, in structure 4, even if/when donor is the oxygen of the six membered ring, the geometrical parameters are almost identical to those of structure 3, when donor is the oxygen of the five membered ring donor and acceptor are closer and the structure is less far from the ideal linearity. In structure 1, this kind of interaction is impossible: the alcoholic hydrogen remains closer to the nearest ester oxygen present on the same ring, but the structure is too far from the linearity required to have a significant stabilization. Finally, the equatorial position of the substituents in structure 2 does not allow this kind of interaction.

Thus, on the basis of these data we can state that there are two factors that affect the stability of isomers 1–4: (a) the ring size, the five-membered ring is more stable than the six-membered ring; (b) the intramolecular hydrogen bonding which increases stability. In six-membered rings, the possibility to give intramolecular hydrogen bonding overcomes the boat–chair stability difference. Six-membered and five-membered rings have similar energy: the energetic difference between 1 and 3 is only 2.40 kcal/mol. In 4, the switch from five to six membered of one ring is slightly overcompensated by the better intramolecular hydrogen bonding stabilization due to its peculiar geometric structure. Interior hydrogen bond stabilization can occur in 1 and 2, but this goes against both entropy and electrostatic repulsion.

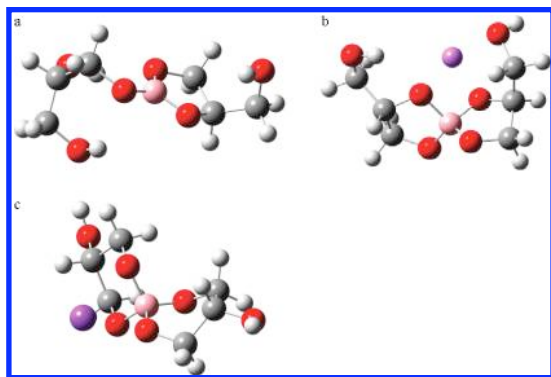


**Figure 3.** Geometrical structures of ions 1–4. Structure 1 has intraring hydrogen bonds. Structure 2 has non-hydrogen bonds. Structures 3 and 4 have inter-ring hydrogen bonds, but in the case of 4 one of these has a more linear structure and thus higher bond energy.

**TABLE 2: Energetic and Geometrical Quantities for Ions and Ionic Pairs Calculated at the B3LYP/CEP-121G(d,p) Level<sup>a,b</sup>**

structure	ion		ionic pair					imaginary frequencies	
	$\Delta E_r$ kcal/mol	H-bond length (Å) and angles (deg)	M <sup>+</sup>	$R(M-O)$ (Å)	$\Delta E_r$ (kcal/mol)	$\Delta E_f$ (kcal/mol)	$\Delta E_{TS}$ (kcal/mol)	Im( $\omega$ ) cm <sup>-1</sup>	
two five-membered rings	0.12	$R(O-H) = 2.120$ Å	H <sup>+</sup>	0.97	0.00	-325.89	32.24	1288	
			Li <sup>+</sup>	1.87	0.00	-154.58			
			Na <sup>+</sup>	2.24	0.00	-128.95			
two six-membered rings (chair)	10.39	$A(H-O-H) = 118.8$	H <sup>+</sup>	0.97	5.40	-330.67	33.09	1385	
			Li <sup>+</sup>	1.68	0.90	-163.80			
			Na <sup>+</sup>	2.19	11.04	-128.18			
two six-membered rings (boat)	2.40	$R(O-H) = 1.807$ Å	H <sup>+</sup>	0.97	1.09	-327.05	23.78	1253	
			Li <sup>+</sup>	1.80	4.30	-152.59			
			Na <sup>+</sup>	2.19	5.86	-125.42			
one five-membered and one six-membered (boat) ring	0.00	$R(O-H) = 1.782$ Å (a)	H <sup>+</sup>	0.97	0.95	-324.83	27.48	1311	
			$A(H-O-H) = 164.6$ (a)	Li <sup>+</sup>	1.80	5.06	-149.48		
			$R(O-H) = 1.807$ Å (b)						
		$A(H-O-H) = 155.1$ (b)	Na <sup>+</sup>	2.18	5.82	-123.10			

<sup>a</sup> Donor from five-membered ring and acceptor from a six-membered ring. <sup>b</sup> Vice versa. The imaginary frequencies refer to transition vectors.



**Figure 4.** Some structures of the ionic pairs. (a) Isomer 4 with H<sup>+</sup>, (b) isomer 1 with Li<sup>+</sup>, and (c) isomer 3 with Na<sup>+</sup>.

Starting from the anion structures we considered the corresponding ionic pairs, taking into account their interaction with H<sup>+</sup>, Li<sup>+</sup>, and Na<sup>+</sup>. Data about these complexes are reported in the right part of Table 2 and in Figure 4. As a general trend, we can state that in the presence of the cation the energetic differences among anionic isomers are smaller than in the case of the isolated anions. Moreover, we observed an inversion in the stability order: five-membered structures are more stable than the hybrid ones.

In agreement with the experimental results, hydrogen has a completely different behavior with respect to the other cations. Whereas sodium simply coordinates itself on the tetrahedral center without a significant alteration of the geometry with respect to the “nude” anion, hydrogen affects the stability of the chelate anions converting the central tetrahedral boron atom in a trigonal one. The four central oxygen atoms are practically immobile but the boron atom moves away from the oxygen approached by the proton. Moreover, the proton moves from an oxygen atom to another one via a first-order transition state.

The barrier energies and the transition frequencies for the different isomers are reported in Table 2, the structure of the transition state for the isomer 4 is reported in Figure 4. The transition vectors are very similar as are the associated frequencies. Almost all motions are concentrated on hydrogen and boron atoms: they move in nearly opposite directions. An animation showing the motion of the transition state along the transition vector is reported in Supporting Information.

For Li[G<sub>1</sub>B] and Na[G<sub>1</sub>B] we are not able to find transition states. For these salts, the cation is generally positioned between two boric ester oxygen atoms (see Figure 4b), except in the

two chair six-membered ring isomers where Li<sup>+</sup> is coordinated to a single oxygen and Na<sup>+</sup> is bridged with three oxygen atoms (Figure 4c).

Structure 2 with lithium as counterion is therefore similar to H[G<sub>1</sub>B]. In this isomer none of the four central oxygen atoms is involved in a hydrogen bond, and lithium does not have to compete with alcoholic hydrogens to coordinate. Apart from this exception, Li[G<sub>1</sub>B] and Na[G<sub>1</sub>B] are simply ionic pairs.

At variance, H[G<sub>1</sub>B] represents a completely different situation. The geometries of the different isomers are more similar to those of a covalent compound than to an ionic one: the distance H–O is 0.97 Å; this value is typical for a covalently bonded hydrogen. However, the isomerization barrier is too low for a process occurring through the break of a covalent bond. The situation of H[G<sub>1</sub>B] is therefore dynamic: the proton jumps from an oxygen to another one passing throughout a transition state with a bridged structure whereas the boron atom moves in its cage constituted by the four oxygen atoms in the opposite direction. It is noteworthy that the transition state of H[G<sub>1</sub>B] is very similar to the energetic minima of Li[G<sub>1</sub>B] and Na[G<sub>1</sub>B]. Therefore, near the transition state H[G<sub>1</sub>B] is an ionic pair, whereas near the minima it is a neutral molecule. Furthermore, H[G<sub>1</sub>B] is not a rigid compound: hydrogen and boron atoms are delocalized in a finite and well-defined portion of space instead to perform small oscillations about a given point. The absence of species able to complex the proton, like water, coerces it to compete with boron for the oxygen atoms leading to a dynamic situation. Probably, the bigger lithium and sodium ions are not able to do this leading to more conventional ionic pairs.

## Conclusions

In conclusion, Na<sup>+</sup>, Li<sup>+</sup>, and K<sup>+</sup> based ILs can be prepared from glycerol, boric acid, and the corresponding hydroxides. This reaction allows to obtain also bis(glycerol)borates bearing organic cations. The stability of the bis(glycerol)borate complexes depends by the environment and by the nature of the counterion; in the presence of water the bis(glycerol)boric acid dissociates to the reagents whereas bis(glycerol)borates having as counterion organic or inorganic cations partially hydrolyze to the corresponding mono(glycerol)borates. The tendency of these salts to give in the presence of water the corresponding mono(glycerol)borates reduces the possibility of application in aqueous media but assures, at the same time, a rapid decomposition of the anion in the aquatic environment to well know

compounds (glycerol and boric acid) at the end of the life-cycle when eventually used as solvents or materials.

On the other hand, NMR data of these salts in organic solvents evidence a very low (if any) tendency to hydrolyze confirming the possibility to use them in water free conditions. NMR data evidence also the occurrence of dynamic processes under these conditions, probably the slow interconversion between bis(glycerol)borate isomers. Theoretical calculations confirm a dynamic nature of these ions and ionic pairs. The  $\text{H}[\text{Gly}_2\text{B}]$  structures present minima characterized by a trigonal boron atom and an open ring. Probably, although we have not investigated this aspect, these latter structures can allow an easy isomerization between five- and six- (in boat conformation) membered rings.  $\text{Li}[\text{Gly}_2\text{B}]$  and  $\text{Na}[\text{Gly}_2\text{B}]$  are more traditional ion pairs, and interconversion is probably much slower although not impossible.

## Experimental section

**Measurements.**  $^1\text{H}$  NMR measurements were conducted on a Bruker Advance II 250 spectrometer operating at 250 MHz, and  $\text{D}_2\text{O}$  was used as solvent.  $^{11}\text{B}$   $^1\text{H}$  NMR spectra were recorded on a Varian Gemini 200 BB instrument operating at 64.167 MHz; frequencies are referenced to  $\text{CFCl}_3$ . FT-IR spectra were taken on pure compounds using a Perkin-Elmer Spectrum One FTIR-ATR (400–4000  $\text{cm}^{-1}$ ). Glass transition ( $T_g$ ), crystallization ( $T_c$ ), melting ( $T_m$ ), and decomposition ( $T_d$ ) temperatures were determined from differential scanning calorimetry (DSC) measurements under inert atmosphere, performed on 7–10-mg samples sealed in aluminum pans under an inert atmosphere. Samples were heated in the  $-50/250$  °C temperature range at 20 °C/min heating and cooling rate. Glass transition temperatures ( $T_g$ ) were measured from the inflection point in the second heating curve. Crystallization and melting enthalpies were evaluated from the integrated areas of melting peaks. Indium and stannous were used as calibration standards. Conductance measurements were performed using a CON 510 bench meter supplied with conductivity/TDS electrode. This electrode comes with stainless steel ring, a cell constant of  $K = 1.0$ , and an inbuilt temperature sensor for automatic temperature compensation. ESI-MS analyses were performed on a Finnigan LCQ Advantage (Thermo Finnigan, San Jose, CA, USA) ion trap instrument equipped with an Excalibur software.

**Synthesis of  $\text{H}[\text{Gly}_2\text{B}]$ .** Boric acid (61.83 g 1 mol) and glycerol (190 g, 2 mol) were added to a 1 L flask. Toluene (500 mL) was added, and the mixture was stirred at 110 °C for 4 h, continuously removing the byproduct water by azeotropic distillation. The final solution was evaporated to remove toluene under vacuum obtaining the glyceroboric acid in a quantitative yield.  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{CD}_3\text{CN}$ ): 67.9, 67.7, 65.3.  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ .  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3339, 2922, 1476, 1407, 1323, 1276, 1171, 1109, 1031, 977, 923, 833.

**Synthesis of  $\text{M}[\text{Gly}_2\text{B}]$  ( $\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Li}^+$ ).** To a solution of glyceroboric acid (3.91 g, 20 mmol) in 50 mL of  $\text{H}_2\text{O}$ , potassium hydroxide (1.15 g, 20 mmol) was added. The mixture was stirred at 100 °C for 4 h. The solvent was removed under vacuum obtaining the corresponding salts.

**$\text{K}[\text{Gly}_2\text{B}]$ .**  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{D}_2\text{O}$ ): 72.6, 63.4 ppm. By dilution, we observed the appearance of other peaks, two of which attributable to glycerol (71.9 and 62.3).  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ . IR:  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3257, 2920, 2867, 1037, 944.

**$\text{Na}[\text{Gly}_2\text{B}]$ .**  $^{11}\text{B}$  NMR (64 MHz,  $\text{D}_2\text{O}$ ): 10.66 ppm. On standing in  $\text{D}_2\text{O}$  we observed the appearance of another peak at 6.6 ppm attributable to  $[\text{GlyB}(\text{OH})_2]^-$ .  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{D}_2\text{O}$ ): 72.5, 63.5, 63.3. By dilution, we observed the appearance of other peaks, two of which attributable to glycerol (71.9 and

62.3).  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ . IR:  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3235, 2914, 2865, 1658, 1067, 1038, 1012, 940.

**$\text{Li}[\text{Gly}_2\text{B}]$ .**  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{D}_2\text{O}$ ): 72.5, 63.5, 63.3. By dilution, we observed the appearance of other peaks, two of which attributable to glycerol (71.9 and 62.3).  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ . IR:  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3217, 2926, 2868, 1658, 1083, 1014, 942, 907.

**Synthesis of  $[(\text{Bu})_4\text{N}][\text{Gly}_2\text{B}]$ .** To a solution of glyceroboric acid (5 mmol) in 10 mL of  $\text{H}_2\text{O}$ ,  $[(\text{Bu})_4\text{N}]\text{OH}$  (1.15 g, 5 mmol) was added. The mixture was stirred at 100 °C for 3 h. The solvent was removed under vacuum obtaining the corresponding salt.

**$[(\text{Bu})_4\text{N}][\text{Gly}_2\text{B}]$ .**  $^{11}\text{B}$  NMR (64 MHz,  $\text{D}_2\text{O}$ ): 12.9 (br) ppm. By dilution, we observed the presence of two sharp peaks at 10.8 and 6.8 ppm attributable, respectively, to  $[(\text{Bu})_4\text{N}][\text{Gly}_2\text{B}]$  and  $[\text{GlyB}(\text{OH})_2]^-$ .  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{DMSO}_{d6}$ ): 73.1 (br), 65.5 (br), 57.5, 23.1, 19.2, 13.4.  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{D}_2\text{O}$ ): 72.4, 63.5, 63.3, 57.5, 22.6, 18.7, 12.4. By dilution, we observed the appearance of other two peaks attributable to glycerol (71.9 and 62.3).  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ ;  $m/z$  ESI-MS (+): 242.0  $[(\text{Bu})_4\text{N}]^+$ ; 675.0  $[(\text{Bu})_4\text{N}]_2[\text{Gly}_2\text{B}]^+$ ; 619  $[(\text{Bu})_4\text{N}]_2-[\text{GlyB}(\text{OH})_2]^+$ . IR:  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3235, 2914, 2865, 1658, 1067, 1038, 1012, 940.

**Synthesis of  $[\text{bmim}][\text{Gly}_2\text{B}]$ .** To a solution of glycerol (22 g, 24 mmol), boric acid (0.74 g, 12 mmol), and  $\text{Li}_2\text{CO}_3$  (0.88 g, 12 mmol) in 10 mL of  $\text{H}_2\text{O}$   $[\text{bmim}][\text{Br}]$  (2.63 g, 12 mmol) was added. The mixture was stirred at 60 °C for 6 h and after cooling at room temperature, water was removed at reduced pressure. Undissolved  $\text{LiBr}$  was separated from the viscous uncoloured liquid by centrifugation. The residue oil, containing  $[\text{bmim}][\text{Gly}_2\text{B}]$  and dissolved  $\text{LiBr}$  was analyzed by NMR and ESI-MS.

**$[\text{bmim}][\text{Gly}_2\text{B}]$ .**  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{CD}_3\text{CN}$ ): 137.4, 124.4, 123.0, 65.8 (br), 49.4, 36.6, 32.5, 19.8, 13.5.  $^{13}\text{C}$  NMR (67.5 MHz,  $\text{D}_2\text{O}$ ): 137.4, 124.4, 123.0, 72.6, 63.6, 49.2, 36.6, 32.3, 19.8, 13.2.  $^{11}\text{B}$  NMR (64 MHz,  $\text{D}_2\text{O}$ ): 10.5 ppm. By dilution, we observed the appearance of another peak at 6.5 ppm attributable to  $[\text{GlyB}(\text{OH})_2]^-$ .  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ ; 139  $[\text{bmim}]^+$ .

**Synthesis of  $[\text{HOetmim}][\text{Gly}_2\text{B}]$ .** To a solution of  $[\text{HOetmim}][\text{Cl}]$  (12.1 g, 75 mmol) in acetonitrile–water (100 mL, 9:1) an equimolar amount of  $\text{Na}[\text{Gly}_2\text{B}]$  (16.05 g, 75 mmol) was added. The mixture was stirred for 12 h at room temperature; the solvent was removed at reduced pressure, and the undissolved  $\text{NaCl}$  was separated from the viscous uncoloured liquid by centrifugation. The residue oil, containing  $[\text{HOetmim}][\text{Gly}_2\text{B}]$  and dissolved  $\text{NaCl}$ , was analyzed by NMR and ESI-MS.

**$[\text{HOetmim}][\text{Gly}_2\text{B}]$ .**  $\delta_{\text{H}}$  (250 MHz,  $\text{DMSO}_{d6}$ ): 3.25–3.54 (10H, m) 3.59 (2H, t,  $\text{CH}_2\text{O}$ ), 3.60 (s 3H,  $\text{CH}_3\text{N}$ ) 4.20 (2H, m,  $\text{HOCH}_2\text{CH}_2\text{N}$ ), 7.22 (1H, s,  $\text{N}-\text{CH}=\text{CH}$ ), 7.71 (1H, s,  $\text{N}-\text{CH}=\text{CH}$ ), 9.10 (1H, s,  $\text{N}=\text{CH}-\text{N}$ ).  $^{13}\text{C}$  NMR (63 MHz,  $\text{DMSO}_{d6}$ ): 136.2, 123.4, 122.7, 72.6 (br), 62.8 (br), 59.4, 51.6, 35.6.  $^{13}\text{C}$  NMR (63 MHz,  $\text{D}_2\text{O}$ ): 136.2, 123.4, 122.1, 72.6, 63.6, 59.6, 51.4, 35.6.  $^{11}\text{B}$  NMR (64 MHz,  $\text{D}_2\text{O}$ ): 10.9 ppm. By dilution, we observed the appearance of another peak at 6.8 ppm attributable to  $[\text{GlyB}(\text{OH})_2]^-$ .  $m/z$  ESI-MS (–): 191.0  $[\text{Gly}_2\text{B}]^-$ ; 451.0  $[\text{HOetmim}][\text{Gly}_2\text{B}][\text{GlyB}(\text{OH})_2]^-$ .  $m/z$  ESI-MS (+): 127 (100%)  $[\text{HOemim}]^+$ , 289 (15%)  $[\text{HOemim}]_2\text{Cl}^+$  (due to the presence of residual chloride).

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**Supporting Information Available:** Absolute electronic energies with zero-point corrections, molecular geometries, transition vectors, animation of the transition vector for isomer I are available as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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